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Single Crystal X-Ray Diffraction Studies on Magnetic $Yb_5Co_4Ge_{10}$[*]

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ABSTRACT

The high quality single crystals of $Yb_5Co_4Ge_{10}$ have been grown by the indium metal flux method and characterized by means of single crystal X-ray diffraction data. $Yb_5Co_4Ge_{10}$ crystallizes in the $Sc_5Co_4Si_{10}$ structure type, tetragonal space group *P*4/*mbm* and lattice constants are $a = b = 12.6369(18)$ Å and $c = 4.1378(8)$ Å. Crystal structure of $Yb_5Co_4Ge_{10}$ composed of three-dimensional $[Co_4Ge_{12}]$ network having five, six and eight membered rings. The three non-equivalent Yb atoms are sandwiched in three different channels created by the $[Co_4Ge_{12}]$ network. Based on the bond length analysis from the crystallographic information, we confirmed that Yb1 and Yb2 atoms are in the trivalent magnetic state and Yb3 is in the divalent non-magnetic state.

Keywords: X-Ray Diffraction; Single Crystal; Intermetallics; Ytterbium

1. Introduction

The ternary intermetallic compounds of general formula $RE_5T_4X_{10}$ (*RE* = rare earths; T = Co, Ni, Rh, Ir and Os and X = Si, Ge, Sn) have been reported mostly for their interesting physical properties [1-22]. These compounds crystallize in the tetragonal $Sc_5Co_4Si_{10}$ structure type having *P*4/*mbm* space group [1]. As per Pearson crystallographic database [23] and inorganic crystal structure database [24], there are 37 compounds reported within the family of $RE_5T_4X_{10}$ compounds and are listed in **Table 1**. Among them only three were studied for the crystal structure from the single crystal XRD data, including our recent discovery of $Yb_5Ni_4Ge_{10}$ mixed valent Yb atoms [2]. However, the majority of these compounds were studied for their physical properties. For examples, the non-magnetic $RE_5T_4X_{10}$ (*RE* = rare earths; T = Co, Rh, Ir, and Os; X = Ge, Si) compounds were reported as superconductors at low temperatures [5,12,17-19]. The $RE_5Rh_4X_{10}$ (*RE* = Gd, Tb, Dy, Ho, Er, Tm; X = Si, Ge, Sn) and $Dy_5Ir_4Si_{10}$ compounds were reported for their interesting magnetic properties and all of them order either ferromagnetically or antiferromagnetically at low temperature [11,18,20,21].

Katoh *et al*. synthesized the $Yb_5Co_4Ge_{10}$ compound in the polycrystalline nature using Bridgman method [22]. They have proposed the mixed valent nature of Yb in $Yb_5Co_4Ge_{10}$ based on the magnetic susceptibility data. In order to understand the structure-property relationship, we need to study the complete crystallography analysis from a high quality single crystal. The chemical bonding nature obtained from the crystal structure can be used to explain the valency of the Yb atoms. Recently, molten metal fluxes have been used as an excellent alternative to the conventional synthetic methods for the exploratory synthesis of new rare earth intermetallic compounds, as well as single crystal growth of already reported compounds [25-39].

In this paper, we report the single crystal growth of $Yb_5Co_4Ge_{10}$ using liquid indium metal flux technique. The crystal structure of this compound has refined from the single crystal XRD data. We also discuss the crystal structure and chemical bonding of $Yb_5Co_4Ge_{10}$ and compared with other compounds.

2. Experimental Section

2.1. Synthesis

The following reagents were used as purchased without further purification: Yb (in the form of metal pieces cut from metal chunk, 99.99% Alfa Aesar), Co (powder,

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Table 1. The list of the $RE_5T_4X_{10}$ (*RE* = Rare earth, T = Co, Rh, Ir, Os and Ni; *X* = Si, Ge and Sn) compounds reported.

Compound	*a* (Å)	*c* (Å)	Vol. ($Å^3$)	Ref.
$Y_5Os_4Ge_{10}$	13.012 (4)	4.2927 (4)	726.8	[3,4]
$Gd_5Rh_4Ge_{10}$	12.987 (8)	4.299 (3)	725.0	[5]
$Dy_5Os_4Ge_{10}$	13.034 (2)	4.299 (3)	725.8	[6]
$Ho_5Os_4Ge_{10}$	12.984 (3)	4.2820 (6)	721.9	[7,8]
$Ho_5Os_4Ge_{10}$	12.984 (3)	4.2820 (6)	721.9	[9]
$Er_5Rh_4Ge_{10}$	12.889 (8)	4.236 (3)	707.7	[5]
$Er_5Ir_4Ge_{10}$	12.865 (9)	4.278 (3)	694.8	[5]
$Tm_5Co_4G_{10}$	12.622 (9)	4.139 (4)	659.4	[5]
$Tm_5Rh_4Ge_{10}$	12.868 (9)	4.230 (3)	700.4	[5]
$Tm_5Ir_4Ge_{10}$	12.846 (8)	4.267 (3)	704.1	[5]
$Yb_5Co_4G_{10}$	12.645 (9)	4.138 (4)	661.6	[5]
$Yb_5Co_4G_{10}$	12.637 (2)	4.1378 (8)	660.7	*
$Yb_5Ni_4G_{10}$	12.672 (2)	4.1598 (8)	667.9	[2]
$Yb_5Rh_4Ge_{10}$	12.886 (9)	4.234 (3)	703.0	[5]
$Yb_5Ir_4Ge_{10}$	12.877 (9)	4.285 (3)	710.5	[5]
$Lu_5Co_4G_{10}$	12.606 (8)	4.125 (3)	655.5	[5]
$Lu_5Rh_4Ge_{10}$	12.850 (80	4.208 (3)	694.8	[5]
$Lu_5Ir_4Ge_{10}$	12.831 (9)	4.252 (3)	700.0	[5]
$Sc_5Co_4Si_{10}$	12.013 (3)	3.936 (2)	568.0	[10]
$Sc_5Co_4Si_{10}$	12.01 (1)	3.936 (5)	567.7	[1]
$Sc_5Rh_4Si_{10}$	12.344 (2)	4.039 (1)	615.4	[11]
$Sc_5Rh_4Si_{10}$	12.330 (3)	4.030 (2)	612.6	[1]
$Sc_5Ir_4Si_{10}$	12.335 (2)	4.083 (1)	621.2	[1,11]
$Y_5Ir_4Si_{10}$	12.599 (2)	4.234 (3)	672.0	[12]
$Dy_5Ir_4Si_{10}$	12.577 (2)	4.234 (1)	670.2	[13,14]
$Ho_5Ir_4Si_{10}$	12.558 (2)	4.218 (1)	665.1	[13]
$Er_5Ir_4Si_{10}$	12.540 (2)	4.208 (1)	661.7	[13]
$Tm_5Ir_4Si_{10}$	12.513 (2)	4.197 (1)	657.1	[13]
$Yb_5Ir_4Si_{10}$	12.503 (3)	4.182 (2)	653.7	[13]
$Lu_5Rh_4Si_{10}$	12.502 (2)	4.137 (2)	646.6	[1]
$Lu_5Ir_4Si_{10}$	12.475 (2)	4.171 (1)	649.1	[1]
$La_5Ir_4Sn_{10}$	14.088 (10)	4.690 (4)	930.8	[15]
$Ce_5Rh_4Sn_{10}$	14.053 (12)	4.621 (5)	912.5	[15]
$Ce_5Ir_4Sn_{10}$	14.027 (15)	4.648 (8)	914.5	[15]
$Pr_5Rh_4Sn_{10}$	14.035 (13)	4.612 (4)	908.4	[15]
$Pr_5Ir_4Sn_{10}$	13.993 (16)	4.632 (6)	906.9	[15]
$Nd_5Rh_4Sn_{10}$	13.992 (17)	4.588 (7)	898.2	[15]
$Sm_5Rh_4Sn_{10}$	13.926 (16)	4.554 (6)	883.1	[15]
$Ho_5Rh_4Ge_{10}$	12.9336 (9)	4.2596 (6)	712.5	[16]

*This work.

99.99% Alfa Aesar), Ge (pieces, 99.999% Alfa Aesar) and In (shots, 99.99% Alfa-Aesar). High quality single crystals of $Yb_5Co_4Ge_{10}$ were obtained by combining ytterbium metal (0.3 g), cobalt powder (0.1 g), germanium (0.3) and indium shots (2 g) in an alumina crucible. The crucible was placed in a 13 mm fused silica tube which was flame sealed under a vacuum of 10^{-5} torr, to prevent oxidation during heating. The reactants were then heated to 1173 K over 8 h, and maintained at that temperature for 2 h to allow proper homogenization, then cooled down to 1073 K in 2 h and kept at this temperature for 72 h. Finally, the sample was allowed to cool slowly to 303 K over 48 hrs. No reactions with the alumina crucible material could be detected. The reaction product was isolated from the excess indium flux by heating at 673 K and subsequently centrifuging through a coarse frit. Any remaining flux was removed by immersion and sonication in glacial acetic acid for 24 h. The final crystalline product was rinsed with water and dried with acetone. A few small gray rod-shaped crystals of $Yb_5Co_4Ge_{10}$ carefully selected for the elemental analysis and single crystal XRD data collection. $Yb_5Co_4Ge_{10}$ is stable in air and no decomposition was observed even after several months.

2.2. Elemental Analysis

Semi-quantitative microanalyses were performed on the single crystals obtained from the flux techniques using a scanning Leica 220i electron microscope (SEM) equipped with Bruker 129 eV energy dispersive X-ray analyzer (EDS). Data were acquired with an accelerating voltage of 20 kV and in 60 s accumulation time. The EDS analysis performed on visibly clean surfaces of the single crystals obtained from the flux method indicated that the atomic composition was close to 5:4:10 in good agreement with the composition obtained from the single crystal data refinement. A typical SEM image of rod-like crystals of $Yb_5Co_4Ge_{10}$ grown from the flux synthesis is shown in **Figure 1**.

2.3. Single Crystal X-Ray Diffraction

Single crystal structural data of $Yb_5Co_4Ge_{10}$ was collected at room temperature on rod shaped single crystals using a Bruker Smart-CCD diffractometer equipped with

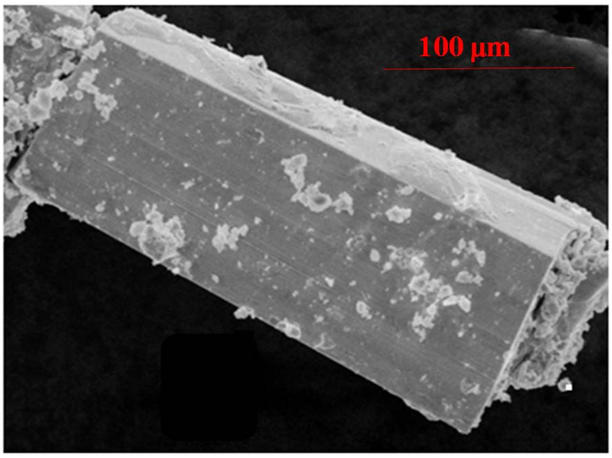

Figure 1. Typical SEM image of $Yb_5Co_4Ge_{10}$ single crystal grown from In flux.

a normal focus, 2.4 kW sealed tube X-ray source with graphite monochromatic Mo-Kα radiation (λ = 0.71073 Å) operating at 50 kV and 30 mA, with ω scan mode. A crystal of suitable size (0.5 × 0.05 × 0.05 mm) was cut from a small rod shape crystal and mounted on a thin glass (~0.1 mm) fiber with commercially available super glue. A full sphere of 60 frames was acquired up to 57.87° in 2θ. The individual frames were measured with w steps of 0.50° and an exposure time of 20 s per frame. The programme SAINT [40] was used for integration of diffraction profiles and absorption correction was made with SADABS programme [41]. The systematic absences were leading to the centrosymmetric space group *P*4/*mbm*. However, the Platon program within WinGx system, ver. 1.80.05 [42] was used to check the additional symmetry, and this was not suggesting any additional symmetry. The structure was solved by SHELXS 97 [43] and refined by a full matrix least-squares method using SHELXL [44] with anisotropic atomic displacement parameters for all atoms. Packing diagrams were generated with Diamond [45]. In order to check for the correct composition, the occupancy parameters were refined in a separate series of least-squares cycles. All bond lengths are within the acceptable range compared to the theoretical values. Details of the crystallographic data are given in **Tables 2** to **5**.

Table 2. Crystal data and structure refinement for $Yb_5Co_4Ge_{10}$.

Formula weight	1826.82
Temperature	293 (2) K
Wavelength	0.71073 Å
Crystal system	Tetragonal
Space group	*P*4/*mbm*
Unit cell dimensions	*a* = 12.6369 (18) Å *b* = 12.6369 (18) Å *c* = 4.1378 (8) Å
Volume, Z	660.77 (2) $Å^3$, 2
Density (calculated)	9.18118 g/cm^3
Absorption coefficient	62.152 mm^{-1}
F (000)	1556
Crystal size	0.05 × 0.01 × 0.01 mm^3
θ range	2.28° to 28.93°
Index ranges	$-16 \le h \le 17, -17 \le k \le 17, -5 \le l \le 3$
Reflections collected	6117
Independent reflections	526
Completeness to θ = 28.93°	100%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	526/0/34
Goodness-of-fit	1.076
Final *R* indices [>2σ(I)]^a	R_{obs} = 0.0293, wR_{obs} = 0.0671
Extinction coefficient	0.00082 (15)
Largest diff. peak and hole	2.327 and −1.878 e·$Å^{-3}$

$^a R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2]/\Sigma[w(|F_o|^4)]\}^{1/2}$ and calc $w = 1/[\sigma^2(Fo^2) + (0.0318P)^2 + 111.1197P]$ where $P = (Fo^2 + 2Fc^2)/3$.

Table 3. Atomic coordinates (×10^4) and equivalent isotropic displacement parameters ($Å^2$ × 10^3) for $Yb_5Co_4Ge_{10}$ at 296(2) K with estimated standard deviations in parentheses.

Label	x	y	z	U_{eq}*
Yb1	0	0	0	6 (1)
Yb2	1762 (4)	6762 (4)	5000	6 (1)
Yb3	6113 (4)	1113 (4)	5000	7 (1)
Co	2453 (1)	255 (1)	0	5 (1)
Ge1	688 (1)	5688 (1)	0	6 (1)
Ge2	1554 (1)	1991 (1)	0	8 (1)
Ge3	1640 (1)	56 (1)	5000	8 (1)

*U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4. Anisotropic displacement parameters ($Å^2$ × 10^3) for $Yb_5Co_4Ge_{10}$ with estimated standard deviations in parentheses.

Label	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Yb1	7 (3)	7 (3)	4 (1)	0	0	0
Yb2	7 (3)	7 (3)	3 (1)	−1 (1)	0	0
Yb3	8 (3)	8 (3)	5 (4)	−1 (1)	0	0
Co	6 (1)	6 (1)	4 (1)	−1 (1)	0	0
Ge1	7 (5)	7 (5)	5 (1)	−1 (1)	0	0
Ge2	6 (1)	8 (1)	11 (1)	0	0	0
Ge3	8 (1)	14 (1)	3 (1)	−2 (1)	0	0

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + \cdots + 2hka^*b^*U_{12}]$.

Table 5. Selected bond lengths [Å] for $Yb_5Co_4Ge_{10}$ at 296(2) K with estimated standard deviations in parentheses.

Label	Distances	Label	Distances
Yb1-Ge3	2.9300 (9)	Yb3-Co	3.2487 (12)
Yb1-Co	3.1167 (15)	Co-Ge3	2.3232 (9)
Yb2-Ge1	2.8217 (12)	Co-Ge2	2.3603 (19)
Yb2-Ge3	2.9527 (13)	Co-Ge1	2.4112 (17)
Yb2-Ge2	2.9814 (10)	Ge1-Ge1	2.4620 (3)
Yb2-Co	2.9815 (11)	Ge2-Ge2	2.5980 (2)
Yb3-Ge1	3.1228 (8)	Ge2-Ge3	2.9362 (12)
Yb3-Ge3	3.2002 (13)	Ge3-Ge3	2.9341 (17)
Yb3-Ge2	3.2137 (11)		

3. Results and Discussion

3.1. Structure Refinement of $Yb_5Co_4Ge_{10}$

The atomic parameters of $Sc_5Co_4Si_{10}$ [1] were taken as starting parameters and the structure was refined using SHELXL-97 (full-matrix least-squares on F^2) [43] with anisotropic atomic displacement parameters for all atoms. As a check for the correct composition, the occupancy parameters were refined in a separate series of least-squares cycles. Our data confirms the previous X-ray powder data [5], but the atomic positions have been refined with higher precision. Single crystals of $Yb_5Co_4Ge_{10}$

from different synthesis batches were used for the data collection. In the first step of refinement on the single crystal data collected shows that $Yb_5Co_4Ge_{10}$ crystallizes in a primitive tetragonal lattice (*P*4/*mbm*) within the $Sc_5Co_4Si_{10}$ type structure and lattice constants are $a = b =$ 12.6369 (18) Å and $c =$ 4.1378 (8) Å. This refinement resulted in seven crystallographical positions (three Yb, one Co and three Ge) in the $Yb_5Co_4Ge_{10}$ structure. The data collection and structure refinement for $Yb_5Co_4Ge_{10}$ are listed in **Table 2**.

The standard atomic positions and isotropic atomic displacement parameters of this compound are collected in **Table 3**. The anisotropic displacement parameters and important bond lengths are listed in **Tables 4** and **5**, respectively. Further information on the structure refinements is available from: Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), by quoting the Registry Nos. CSD-425832.

3.2. Crystal Chemistry of $Yb_5Co_4Ge_{10}$

The crystal structure of $Yb_5Co_4Ge_{10}$ along *c*-axis is shown in **Figure 2**.

$Yb_5Co_4Ge_{10}$ crystallizes in the primitive tetragonal $Sc_5Co_4Si_{10}$ type structure (space group *P*4/*mbm*). Crystal structure of $Yb_5Co_4Ge_{10}$ is composed of a complex $[Co_4Ge_{12}]$ polyanion network with three types of one dimensional channels, showed along the *c*-axis (**Figure 2**), in which Yb atoms are embedded. The cages are shared through the corners of Co and Ge form pentagonal and hexagonal rings and resulted in a three dimensional network. The pentagonal and hexagonal rings are occupied with Yb2 and Yb3 atoms, respectively. These rings are connected through Co and Ge in *ab* plane and resulted in another large 8-membered ring, which is occupied by large Yb1 atoms. A detailed crystal structure description of the compounds crystallizing in the $Sc_5Co_4Si_{10}$ was reported as an example of the $Yb_5Ni_4Ge_{10}$ compound [2].

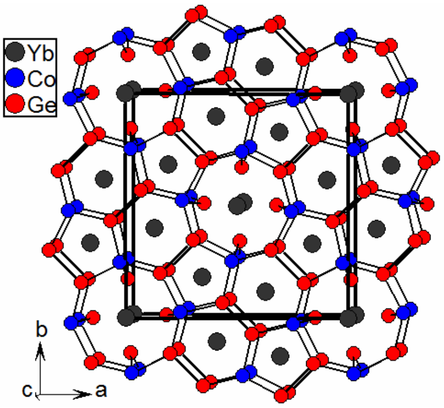

Figure 2. The crystal structure of $Yb_5Co_4Ge_{10}$ as viewed along the *c*-axis; the unit cell is outlined as block solid lines.

Crystallographically there are three different Yb-atoms are present in $Yb_5Co_4Ge_{10}$. All three Yb-coordination environments are significantly different. The Yb1 atom is located at the center of a cage consisting of 12 Ge and 4 Co atoms forming a cage as $Yb[Ge_{12}Co_4]$, Yb2 atoms are surrounded by eight Ge and four Co forming as Yb $[Ge_8Co_4]$ and Yb3 atoms are surrounded by fourteen atoms, $Yb[Ge_{10}Co_4]$. The Yb-Ge and Yb-Co bond lengths in $Yb_5Co_4Ge_{10}$ are in the wide range (2.8218 (9) Å to 3.2138 (10) Å for Yb-Ge and 2.9815 (11) Å to 3.2488 (12) Å for Yb-Co) due to the different size of Yb coordination environments. The average distance obtained for Yb3-Co, 3.2488 (12) Å, is longer than the corresponding distance for Yb1-Co and Yb2-Co with 3.1167 (16) and 2.9815 (11) Å, respectively. Similarly, the average bond distance for the Yb3-Ge is 3.1754 Å, is also longer than the corresponding distance for Yb1-Ge and Yb2-Ge with 3.0175 and 2.9343 Å, respectively. Similar kinds of bonding behavior were observed in the mixed valent $Yb_5Ni_4Ge_{10}$ as well [2]. Since Katoh *et al.* observed the mixed valent Yb in $Yb_5Co_4Ge_{10}$ based on the magnetic susceptibility measurements [22], our crystallographic data suggests the Yb1 and Yb2 atoms are mostly in the trivalent state and Yb3 in the divalent state. Considering the fact that divalent Yb is larger in size (1.86 Å) [46,47] compared to trivalent Yb (1.66 Å) [46,47], Yb3 prefer to be in large cage and others (Yb1 and Yb2) are in the smaller cages.

We also compared the covalent radii and the unit cell volume four Yb based compounds reported in this family, as shown in **Figure 3**. The cell volume of the compounds increases as the covalent radii of the transition metals except in case of Co where there is drop in the cell volume. The drop in the cell volume for Co analogue is due to the major contribution of small size trivalent Yb atoms which was already confirmed in the magnetic susceptibility of two compounds where $Yb_5Ni_4Ge_{10}$ has only 78% Yb^{3+} and $Yb_5Co_4Ge_{10}$ has 94% Yb^{3+}.

The comparison of covalent radii in **Figure 3** also suggests that the metals like Fe, Ru, Os, Pt and Pd are

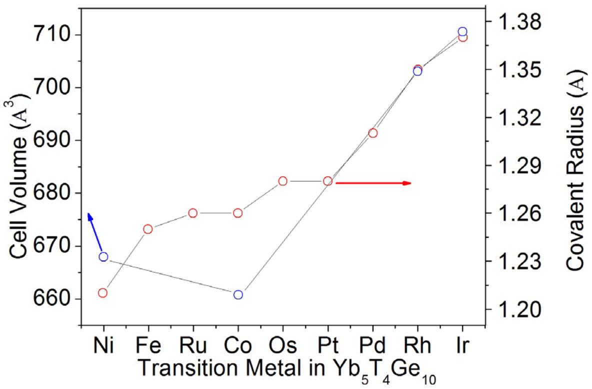

Figure 3. Comparison of the cell volume and covalent radii of transition metals in the $Yb_5T_4G_{e10}$ family.

suitable candidates for the formation $Yb_5T_4Ge_{10}$ compounds because the covalent radii of these metals are within the range of the reported compounds. This assumption can also be supported by the fact that Yb has the ability to show mixed valent compounds to stabilize the compounds.

4. Concluding Remarks

High quality single crystals of $Yb_5Co_4Ge_{10}$ were obtained from the metal flux technique and the crystal structure of $Yb_5Co_4Ge_{10}$ was studied using single crystal X-ray diffraction. Metal flux technique has been proved as vital synthesis method to obtain high quality single crystals. An absolute structure-property relation can be established by understanding the crystal structure from the single crystal X-ray data. Our study opens a lot of scope to find the crystal structure of the compounds which have not been studied as listed in **Table 1** and the synthesis of new compounds as expected based on covalent radii comparison of transition metals.

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